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A METHOD FOR PRODUCING TETRALIN BY SELECTIVE HYDROGENATION  
OF NAPHTHALENE

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#### Description

This invention concerns a method for selective hydrogenation of naphthalene to tetralin in a solvent on a nickel catalyst under mild conditions.

Tetralin is a good solvent for resins and varnishes as well as a valuable starting material for various chemical products. Recently there has been growing interest in tetralin as a hydrogen transfer agent in coal hydrogenation.

An overview of previous methods for production of tetralin can be found in Ullmann's Encyclopedia of Industrial Chemistry [in German], 3rd edition, Vol. 12, p. 589 (1960). Naphthalene of varying purity is used as a starting material without the addition of a solvent.

According to a recent method (US 3541169) naphthalene is stepwise hydrogenated to tetralin in 4-7 successively connected solid bed reactors at 210-290°C. A nickel catalyst containing 0.5-25% nickel oxide (corresponds to about 0.4-19.6% Ni) on a solid support serves as catalyst. According to this patent a higher nickel content causes a decrease of the selectivity.

The hydrogenation of naphthalene to tetralin using complex anionic hydrides of group VIII metals at temperatures up to 150°C is described in US 4224458.

DE-OS 1518558 describes a method for hydrogenation of naphthalene to tetralin that operates at high pressures from 40-300 bar and temperatures up to 300°C on a complex catalyst system that contains nickel, cobalt, molybdenum and tungsten.

The disadvantage of the previous methods for producing tetralin by selective hydrogenation of naphthalene lies in the use of expensive and complicated catalyst systems, in the need for high hydrogen pressures, and in the use of several successively connected hydrogenation reactors, and only nickel catalysts containing under 20 wt% Ni on a solid support can be used in order to achieve high selectivities.

A method was then found for selective catalytic hydrogenation of naphthalene to tetralin at elevated temperature using hydrogen on a nickel/support catalyst, which is characterized by the fact that the catalyst contains 20-60 wt% nickel, with respect to the total weight of the catalyst, and the reaction is carried out in a solvent at 150-250°C and a pressure of 1-20 bar.

The starting material for the method in accordance with the invention is pure naphthalene containing only a few ppm sulfur, for example, up to 30 ppm. Such low-sulfur naphthalene can be obtained, for example, from the cracked middle oil of a steam cracker. Of course, naphthalenes of other origin can also be used, but they have first to be subjected to suitable desulfurization.

Cyclic paraffinic hydrocarbons like cyclohexane, methylcyclohexane, dimethylcyclohexane, ethylcyclohexane, cyclopentane, methylcyclopentane and others are suitable as solvents in the method in accordance with the invention. They are used in amounts such that the naphthalene solution has a concentration of 10-60 wt% naphthalene, with respect to the total solution. The solvent favors heat transfer and guarantees a uniform conduct of the reaction.

In accordance with the invention a nickel-support catalyst containing 20-60 wt% nickel, preferably 25-45 wt% nickel, with respect to the total weight of the catalyst is used. Possibilities as supports are, for example,  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ . Preferably, such supports have an inner surface from 50-250  $\text{m}^2/\text{g}$ , preferably 100-180  $\text{m}^2/\text{g}$ , and a pore volume of 0.2-0.55  $\text{mL}/\text{g}$ , preferably 0.3-0.4  $\text{mL}/\text{g}$ . An  $\text{SiO}_2$  with the said properties, for example, diatomaceous earth, proves to be particularly advantageous as support.

Such a nickel-support catalyst can be produced, for example, by the method of immersion of the support in a nickel salt solution followed by heat treatment.

The prepared catalyst is activated with hydrogen at elevated temperatures of about 150-300°C before the hydrogenation reaction.

The method in accordance with the invention can be conducted, for example, continuously in a fixed bed reactor in liquid phase or in the trickle phase. Pure or technical grade hydrogen, which can contain, for example, up to 20 vol% methane, can be used for hydrogenation.

The reaction is carried out at a pressure of 1-20 bar, preferably 2-10 bar, and a temperature of 150-250, preferably 180-220°C. The naphthalene solution is passed over the said support catalyst in one of the said solvents at a WHSV (= weight hourly space velocity) of 0.3-10 per hour.

The reaction product leaving the reactor is further processed in 2 distillation stages. The pure solvent leaving the top of the first column is returned to the method in accordance with the invention. Tetralin with purity of more than 99% is obtained in the second column from the bottom product of the first column, which contains only tetralin and small amounts of decalin and naphthalene. In the method in accordance with the invention the supplied naphthalene is converted by more than 92% in one pass, and a selectivity of more than 95% is achieved.

#### Example 1:

A solid nickel catalyst containing 35 wt% nickel on an SiO<sub>2</sub> (diatomaceous earth) support is present in a tubular, heatable reactor with a volume of 300 mL. The surface of the catalyst is 120 m<sup>2</sup>/g and the pore volume is 0.4 mL/g. The catalyst is activated with hydrogen at 200°C and atmospheric pressure for 2 h.

A solution of 20 wt% naphthalene in cyclohexane is passed over the activated catalyst at a temperature of 208°C, a pressure of 4.5 bar and a WHSV of 1.3 [h<sup>-1</sup>], with respect to the dilute solution. The solution contains 5 ppm sulfur. The mol ratio of hydrogen to naphthalene is 3:1. A conversion of 95% and selectivity of 97.1% are obtained.

#### Example 2:

A 22% solution of naphthalene in cyclohexane is passed over the catalyst as in Example 1 at a temperature of 210°C and a pressure of 6 bar, at a WHSV of 1.7 [h<sup>-1</sup>]. The solution contains 4 ppm sulfur.

The mol ratio of hydrogen to naphthalene is 4:1. A conversion of 92.2% and selectivity of 97.5% are obtained.

## Claims

1. Process for the selective catalytic hydrogenation of naphthalene to give tetraline at an elevated temperature with hydrogen on a nickel supported catalyst, characterised in that the catalyst has 20 to 60% by weight of nickel, based on the total weight of the catalyst, and the reaction is carried out in a solvent at 150 to 250°C and under a pressure of 1 to 20 bar.
2. Process according to Claim 1, characterised in that the catalyst contains 25 to 45% by weight of nickel.
3. Process according to Claims 1 and 2, characterised in that  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  are used as the support.
4. Process according to Claims 1 to 3, characterised in that the support has an inner surface of 50 to 250  $\text{m}^2/\text{g}$  and a pore volume of 0.2 to 0.55  $\text{ml/g}$ .
5. Process according to Claims 1 to 4, characterised in that naphthalene in a cyclic paraffinic solvent is used.
6. Process according to Claims 1 to 5, characterised in that the reaction temperature is 180 to 220°C.
7. Process according to Claims 1 to 6, characterised in that the pressure is 2 to 10 bar.
8. Process according to Claims 1 to 7, characterised in that the WHSV (= *weight, hourly space velocity*) is 0.3 to 10 per hour, based on the solution of the naphthalene in the solvent.